

FORM PCT/1390
REV. 5/93

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NO.
KNIAZEV-1 (PCT)

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

10/019710

INTERNATIONAL APPLICATION NO.
PCT/AT00/00177

INTERNATIONAL FILING DATE
JUNE 28, 2000

PRIORITY DATE CLAIMED
JUNE 29, 1999

TITLE OF INVENTION
COATING METHOD

APPLICANT(S) FOR DO/EO/US
EVGUENI KNIAZEV

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371 (f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau)
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has **NOT** expired.
 - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

PCT/ISA/210 - Int'l. Search Report

Applicant Claims Priority under 35 U.S.C. §119 of Russian Application No. 99113183/12 filed June 19, 1999.
Applicant Claims Priority under 35 U.S.C. §120 of: PCT No. PCT/AT00/00177 filed June 28, 2000.

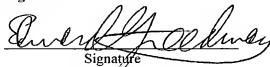
APPLICATION NO. (10/01/97) 10/019710				INTERNATIONAL APPLICATION NO PCT/AT00/00177	ATTORNEY'S DOCKET NO KNIAZEV-1 PCT
<input checked="" type="checkbox"/> The following fees are submitted Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO \$890.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$710.00 Neither international preliminary examination fee paid (37 CFR 1.82) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1,040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$100 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS	PTO USE ONLY
Surcharge of \$130.00 for furnishing the oath or declaration later than ____ 20 ____ 30 months from the earliest claimed priority date (37 CFR 1.492(c))				\$ 890 00	
Claims	Number Filed	Number Extra	Rate		
Total Claims	3 - 20 =	- 0 -	X \$18.00	\$	
Independent Claims	1 - 3 =	- 0 -	X \$84.00	\$	
Multiple dependent claim(s) (if applicable)			+ \$280.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$ 890 00	
Reduction by 1/2 for Small Entity status				\$	
SUBTOTAL =				\$ 890 00	
Processing fee of \$130.00 for furnishing the English translation later than ____ 20 ____ 30 months from the earliest claimed priority date (37 CFR 1.492(f))				\$	
TOTAL NATIONAL FEE =				\$ 890 00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property +				See cover sheet attached to assign \$ to be charged to Deposit Acct	
TOTAL FEES ENCLOSED =				\$ 890 00	
				Amount to be refunded	\$
				charged	\$

____ Applicant claims Small Entity status.

- a. ☒ A check in the amount of **\$890.00** to cover the above fees is enclosed.
 b. ____ Please charge my Deposit Account No. 03-2468 in the amount of \$_____ to cover the above fees. A duplicate
 copy of this sheet is enclosed.
 c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment, to Deposit Account No. 03-2468. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:
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 Roslyn, New York 11576-1696
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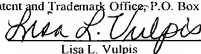

 Signature

Edward R. Freedman
 Reg. No. 26,048

Express Mail No. **EL 871 451 067 US**

Date of Deposit **December 27, 2001**

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, on the date indicated above, and is addressed to BOX PCT, U.S. Patent and Trademark Office, P.O. Box 2327, Arlington, VA 22202.


 Lisa L. Vulpis

PATENTIN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: EVGUENI KNIAZEV-1 (PCT)

PCT No.: PCT/AT00/00177

FILED: JUNE 28, 2000

TITLE: COATING METHOD

PRELIMINARY AMENDMENTBOX PCT

U.S. Patent and Trademark Office

P.O. Box 2327

Arlington, VA 22202

Dear Sir:

Preliminary to Examination, please amend the above-identified application as follows:

IN THE SPECIFICATION

Page 1, after the title, please insert as follows:

--CROSS REFERENCE TO RELATED APPLICATIONS

Applicant claims priority under 35 U.S.C. §119 of Russian Application No. 99113183/12 filed June 29, 1999. Applicant also claims priority under 35 U.S.C. §120 of PCT/AT00/00177 filed June 28, 2000. The international application under PCT article 21(2) was not published in English.--

IN THE CLAIMS

Please amend claim 3 as follows:

3. (Amended) Method as claimed in claim 1, characterised in that electrolytes with a base of hexavalent chromium, nickel, iron, gold and its alloys with cobalt, silver and copper, and copper are used as an electrolyte suspension.

A marked-up version is shown as Exhibit A.

REMARKS

By this Preliminary Amendment, a cross-reference to related applications has been inserted in page 1. Claim 3 has been amended so that the multiple dependency of this claim has been removed to avoid the surcharge associated therewith. No new matter has been introduced. Entry of this amendment is respectfully requested.

Respectfully submitted,
EVGUENI KNIAZEV

By: *Edward R. Freedman*

Allison C. Collard, Reg. No. 22,532
Edward R. Freedman, Reg. No. 26,048
Attorneys for Applicant

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ERF/llv

Enclosure: Exhibit A

EXPRESS MAIL NO. EL 871 451 067 US

Date of Deposit: December 27, 2001

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Lisa L. Vulpis
Lisa L. Vulpis

EXHIBIT A

VERSION WITH MARKINGS TO SHOW CHANGES MADE TO

CLAIM 3

3. (Amended) Method as claimed in [claims 1 and 2] claim 1, characterised in that electrolytes with a base of hexavalent chromium, nickel, iron, gold and its alloys with cobalt, silver and copper, and copper are used as an elecctrolyte suspension.

Coating Method

The invention relates to a method of coating products, in particular decorative veneers, items of jewellery, clocks, tools, etc..

A known method of making products consists in producing a workpiece and then applying a coating to the surface of the workpiece from the electrolyte suspension containing ultra-dispersed diamond-like carbon clusters (see Schebalin A.I., Gubarewitsch W.D., Besedin W.I., Priwalko Ju. N. in Diamant-Chrom-Kompositionsschicht, Explosion, Schlag, Schutz, 1987, 17th edition, p. 111-112, analogy and prototype).

The known method of making products does not take account of the fact that the presence of particles of the ultra-dispersed diamond-like carbon clusters (UDA) from chemical groups of predominantly acid origin on the surface causes the particles of the disperse phase in the electrolytes to behave in a specific way at different pH values. Consequently, the particles of the UDA in acid medium ($\text{pH} < 7$), which is typical of the majority of electrolytes in chrome plating, nickel plating and a few others, receive a negative charge, which impairs their functional capacity on the surface of the cathode, which is also negatively charged. As a result, occlusion of the particles in the coating is negligible. However, it is the nature of the surface of the particles in the UDA which promotes their functional capacity on the cathode.

It is crucial to ensure that the surface of the carbon particles (in the same way as cations) is maintained in the state of the H-form. However, analysis of commercial batches of products available on the market for UDA has shown that the product is in what is referred to as the "salt form".

In technical terms, the intention of this method is to improve the working characteristics of the product whilst using smaller quantities of the expensive UDA product.

This is achieved due to the fact that the main treatment of aqueously suspending the ultra-dispersed diamond-like carbon clusters in an aqueous suspension of sulphuric or hydrochloric acid and then removing the acids in distilled water and the post-treatment by means of a cationically active substance, in order to reduce the volume capacity and re-charge the surface of the

particles in the electrolyte, take place prior to coating.

Substances with a tertiary or quaternary ammonium base are used as the cationically active substance.

As an electrolyte suspension, the electrolytes used are based on hexavalent chromium, nickel, iron, gold and its alloys with cobalt, nickel, silver and copper, and copper.

The essence of the method for making products will be explained in more detail below.

Workpieces were prepared, e.g. in the form of a cylinder of IIIX 15 steel with a hardness $HV = 8.5 \pm 0.2$ GPa. Coatings were applied to the workpieces in a thickness of at least $50 \mu m$ from different electrolytes, in particular electrolytes containing the ultra-dispersed diamond-like carbon clusters (UDA).

Coating was preceded by the main treatment of suspending the ultra-dispersed diamond-like carbon clusters in the aqueous sulphuric or hydrochloric acid solution and then washing out the acids in distilled water and the post-treatment with the cationically active substance to reduce the volume capacity and re-charge the surface of the particles of the electrolyte. Substances with a tertiary or quaternary ammonium base were used as said substance.

Electrolytes on a base of hexavalent chromium, nickel, iron, gold and copper were used as the electrolyte.

The abrasion resistance of the coatings was measured on a system which applies friction by means of a hardened steel or greasing based on the "cylinder with crossing axes" design. The abrasion resistance was determined as a value correlated to the quantity of abraded substance for the specified duration of the tests (the length of the abrasion path) and the friction load applied (for different types of coating, see Table, the absolute friction load for chromium and iron was 15 N, for nickel 10 N, for copper and gold 5N). The sliding speed was 0.78 m/s and the length of the friction path was 140 m. Antibodies were X 12M steel with $HRC_3 = 60 \pm 1$, $R_2 = 0.25-0.32 \mu m$. The microhardness of the coatings was measured by a DMT-3 device under a load of 100g and 50g.

Accordingly, the products made by the specified method were found to have better abrasion resistance and consequently were of higher quality.

In another example, the decorative protective coating is applied in a thickness of 5 μm of a gold-cobalt alloy with a fineness of 985 to the body of a man's wrist watch made from brass C59-1 instead of the usual coating of electrolyte, consisting of gold in the form of a cyanide complex in a quantity of 6.5 g/l, cobalt in the sulphate form in a quantity of 1g/l, tri-substituted aqueous 2-x-potassium citrate in a quantity of 60 g/l and 3g/l of -A-Trilon admixed with "Limeda 30-12" and $\text{UDA}_{\text{treated}} = 10 \text{ g/l}$ to produce a sheen, whilst the electrolyte temperature was 40°C, the current density 0.6 A/dm² and the pH value 4.5.

The abrasion resistance of the coatings was tested on a drum system with an abrasive agent in the form of cylindrical grains of rubber with glass, being 8 mm in diameter and 10 mm in length (sample tested every 10 minutes). The additional test for exposure of the base (brass) was conducted using a 10%-strength chlorine-copper solution (according to the redness of the base). A visual inspection was made under a MBC-2 microscope with 12-times magnification.

The tests were continued until the base was exposed at sharp angles of the watch links.

The results of the tests showed the abrasion resistance of the coating with the treated cluster to be 1.7 times better than the initial cluster. The abrasion resistance of the coating with the initial cluster is 2 times higher than the abrasion resistance of the gold-cobalt coating without UDA. The coating hardness was therefore increased from 2.5 GPa ($\text{UDA}_{\text{initial}}$) to 3.2 GPa ($\text{UDA}_{\text{treated}}$).

The invention therefore improves the working characteristics of the products.

Clearly, the coating method proposed by the invention may also be used for other workpieces, in particular the surfaces thereof. It is possible to coat both all-metal and non-metal workpieces which have been electrolytically treated in acids. For example, the method may be used for spectacle frames, household articles, plastics or similar. Optionally, an additional pre-treatment might be necessary, e.g. in the case of plastics, in order to precipitate a conductive layer onto the respective articles.

Industrial application: The invention may be used for decorative veneers, articles of jewellery, watches and tools, amongst others.

Coating, coating method	Composition of the electrolyte	Abrasion surface, mm ³	Factor of increase in hardness	Hardness, GPa
1	2	3	4	5
Chromium	CrO ₃ -250 g/l; H ₂ SO ₄ -2.5 g/l;			
50 A/dm ²	(pH 1)			
55-57°C	UDA _{initial} -15 g/l	0.18 x 10 ⁻²	1.0	9.5
	UDA _{treated} -15 g/l	0.87 x 10 ⁻³	2.0	9.8
	UDA _{treated} -10 g/l	0.13 x 10 ⁻²	1.4	9.8
	CrO ₃ -250 g/l; K ₂ SiF ₆ -18 g/l; SrSO ₄ -6 g/l;			
	UDA _{initial} -15 g/l	0.15 x 10 ⁻²	1.0	10.5
	same with UDA- treated-15 g/l	0.92 x 10 ⁻³	1.6	12
	same with UDA- treated-8 g/l	0.11 x 10 ⁻²	1.4	11.5
Nickel	NiSO ₄ -270 g/l; NiCl-30 g/l;			
5 A/dm ²	H ₃ BO ₃ -30g/l; (pH=4.5)			
65°C	+UDA _{initial} -20g/l	0.7 x 10 ⁻¹	1.0	2.7
	same			
	+UDA _{treated} -20g/l	0.29 x 10 ⁻¹	2.4	3.8
	same			
	+UDA _{treated} -10g/l	0.52 x 10 ⁻¹	1.34	not measured

Copper	CuSO ₄ -45 g/l; Na ₄ P ₂ O ₇ -160 g/l;			
1.5 A/ dm ²	Na ₂ HPO ₄ -90 g/l; (pH=8.5) + UDA _{initial} -8 g/l + UDA _{treated} -8g/l			
Gold	Au in the form of the cyanide com- plex			
0.6 A/ dm ²	10 g/l; citric acid 35 g/l;			
40°C	Tri-substituted potassium citrate 35 g/l; Sheen agent “Limeda 3C-12” – 1g/l; + UDA _{initial} -10g/l + UDA _{treated} -10g/l	0.19 x 10 ⁻² 0.32 x 10 ⁻²	1.0 1.7	1.89 2.42
Iron	FeSO ₄ -400 g/l; Al(SO ₄) ₃ -100 g/l;			
5 A/ dm ²	(pH=3)			
60°C	+ UDA _{initial} -10g/l + UDA _{treated} -10g/l	0.31 x 10 ⁻¹ 0.21 x 10 ⁻¹	1.0 1.7	4.2 4.9

Claims

1. Method of coating objects with a coating from an electrolyte-suspension containing ultra-dispersed diamond-like carbon clusters, characterised in that the main treatment with aqueous suspension of the ultra-dispersed diamond-like carbon clusters in aqueous sulphuric or hydrochloric acid solution and then washing out the acids in distilled water and the post-treatment by means of a cationically active substance to reduce the volume capacity and re-charge the surface of the particles in the electrolyte take place prior to coating.
2. Method as claimed in claim 1, characterised in that substances with a tertiary or quaternary ammonium base are used as the cationically active substance.
3. Method as claimed in claims 1 and 2, characterised in that electrolytes with a base of hexavalent chromium, nickel, iron, gold and its alloys with cobalt, silver and copper, and copper are used as an electrolyte suspension.

A b s t r a c t

The invention describes a method of making products to improve the working characteristics of a product and is based on the fact that the main treatment of aqueously suspending an ultra-dispersed diamond-like carbon cluster in an aqueous sulphuric or hydrochloric acid solution and then removing the acids in distilled water takes place prior to coating. The technical result of this method is an improvement in the working characteristics of the product whilst using smaller quantities of the expensive UDA product.

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(Includes Reference to PCT International Applications)

ATTORNEY'S DOCKET NUMBER

06 MAY 2002

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Coating Method

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Serial No. _____

on _____

and was amended

on _____ (if applicable).

☒ was filed as PCT international application

Number PCT/AT 00/00177

on 28 June 2000

and was amended under PCT Article 19

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
Russian Federation(RU)	99 113 183/12	29 June 1999	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(Includes Reference to PCT International Applications)

ATTORNEY'S DOCKET NUMBER

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS			STATUS (Check One)		
U.S. APPLICATION NUMBER	U.S. FILING DATE		PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)			

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration numbers):

KURT KELMAN, Registration No. 18,628

ALLISON C. COLLARD, Registration No. 22,532;

EDWARD R. FREEDMAN, Registration No. 26,048

WILLIAM C. COLLARD, Registration No. 38,411

CHRISTOPHER B. GARVEY, Registration No. 31,015

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2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
		<u>Kniazey</u>	<u>Evgueni</u>	
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
		<u>Moskau</u>	<u>Russian Federation</u>	<u>Russian Federation</u>
1	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
		<u>Marschal Zacharov Strasse</u>	<u>RU 115569 Moskau</u>	<u>Russian Federation</u>
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
		<u>Gebaudez, Wohnung 400</u>		
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
2	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201

SIGNATURE OF INVENTOR 202

DATE

DATE